Dehydration of Concentrated Acetic Acid Solutions by Pervaporation Using Novel MER Zeolite Membranes

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(Received December 28, 2006; CL-061519; E-mail: ta.nagase@aist.go.jp)

The dehydration for the 90 wt % acetic acid (AcOH) solution was successfully performed for the first time using novel merlinoite (MER) zeolite membranes. The water selectivity was greater than 8000 by the pervaporation (PV) method. The permeation flux at 40 °C was 0.1 kg m^{-2} h^{-1}. Furthermore, the membranes were stable more than 100 h under acidic conditions of pH 3.4.

Zeolite membranes with low SiO_2/Al_2O_3 ratios (SAR) are highly hydrophilic and can effectively separate water from organic solvents. Currently, the LTA zeolite membranes are commercially available and have been applied for the dehydration of alcohols on a large scale.[1] However, the LTA membranes are unstable in acidic media. The stability of zeolite membrane in the acidic media increases as the SAR of zeolite framework increases, while its hydrophilicity decreases. The development of zeolite membranes with high chemical resistances is essential for extending their range of applications in the separation of industrially valuable materials such as biomass solutions. Recently, some zeolite membranes with medium SARs (mordenite,[2] zeolite T,[3,4]) were investigated for the dehydration of AcOH solutions. For 40–70 wt % AcOH feed solutions at 60–75 °C, the water/AcOH separation factor ($\alpha_{w/AcOH}$) and the fluxes (Q) of the membranes were ca. 1000 and 0.3–0.9 kg m^{-2} h^{-1}, respectively. For 80–90 wt % AcOH solutions, these values decreased to $\alpha_{w/AcOH} = 30$–70 and $Q = 0.03$–0.2 kg m^{-2} h^{-1} due to the association of water and AcOH molecules[2] or pore filling of the membranes by the AcOH molecules.[3] Ying et al. investigated the PV performances of the zeolite T membrane, and the performance for a 90 wt % ethanol (EtOH) solution decreased by immersing in the AcOH solutions.[4] Tanaka et al. tested the long-term stability of the zeolite T membrane by using a 50 wt % AcOH solution at 75 °C.[3] It was observed that the $\alpha_{w/AcOH}$ value decreased to 2/3 of the initial value after immersing it for 4 days.[3] Thus, it appears that mordenite (MOR) and zeolite T membranes are not suitable for the dehydration of concentrated acidic solutions. Previously, we successfully synthesized phillipsite and merlinoite (MER) zeolite membranes on a porous mullite substrates;[5] it was found that these membranes could be applied to the esterification of EtOH and AcOH in concentrated solutions.[6] In this study, the dehydration of concentrated AcOH solutions was performed by employing PV method through the MER membranes. Further, the long-term stability of the membranes under acidic conditions was examined.

The MER membranes were hydrothermally prepared on the outer surfaces of porous mullite tubes (Nikkato Co. SiO_2: 67% and Al_2O_3: 33%, 6 mmφ and 10 mm$\varphi \times 5$ cm, 44% porosity, 2-μm nominal pore diameter).[5] Either K-MER or K-CHA powders were used as seeds and implanted in the macropores of the tubes. The tubular supports were hydrothermally treated at 140 °C for 12 h in the synthesis solutions for bringing about the secondary growth of the seeds. The synthesis solutions were prepared by mixing KOH, NaOH, γ-Al_2O_3, and colloidal silica (Catalysts & Chemical Ind. Co., Ltd., Cataloid SI-30) in the molar compositions of K_2O:Na_2O:Al_2O_3:SiO_2:H_2O = 0.77:0.05:x:1:44.8 ($x = 0.4$–0.8). The resulted SARs of the solutions were 1.3–2.5, respectively. The structures of the membranes were identified by XRD (Bruker axs/Mac Science Co., Ltd, M21X-SRA). The surface observation and chemical analysis of the membranes were carried out by SEM-EDX (Hitachi, S-800, and Horiba, Emax energy EX320). The dehydration performances of the MER membranes were measured by a batch-type PV equipment.[5] One end of the tubular membrane was sealed, while the other one was connected to a stainless-steel tube by using resin (Varian, Torr Seal) coated with polyimide (Kyocera Chemical Co., KEMITITE CT4150) and silicon rubber (Shin-Etsu Chemical Co., Ltd., KE3417) to prevent the dissolution of the resin. The membrane was immersed in aqueous feed solutions, and the inside of the tubular membrane was evacuated by a rotary pump. Since the components permeated through the membrane in the form of vapors, they were collected by a condenser with liquid nitrogen. The recovered solution was analyzed for its composition using gas chromatographs (GC-TCD and GC-FID). The permeation flux and the separation factor were calculated from the weight and composition of the collected permeates, respectively.

Table 1 shows the preparation conditions and the dehydration performances of the membranes for a 95 wt % EtOH solu-

Table 1. Preparation of MER membranes and their dehydration performance for the 95 wt % EtOH solution

Sample Name	Condition for Preparation of MER Membranes				Dehydration Performance for the 95 wt % EtOH Solution at 40 °C	
	Seed	Mullite Supports /mm φ	Seed Amounts /g m^{-2}	SAR of Synthesis Solution	$\alpha_{w/EtOH}$	Q /kg m^{-2} h^{-1}
C6	CHA	6	5.0	1.3	>10000	0.2
6R1	MER	6	1.9	1.3	14	0.1
6R2			3.0		560	0.04
6S1			4.0[a]		6200	0.1
L10R	MER	10	2.5	1.3	2000	0.3
L10S			4.0[a]		5900	0.04
M10R	MER	10	—	1.9	970	0.2
H10R	MER	10	2.9	2.5	70	0.1
H10S			4.1[a]		211	0.1

[a] Seed solution was sucked before rubbing.

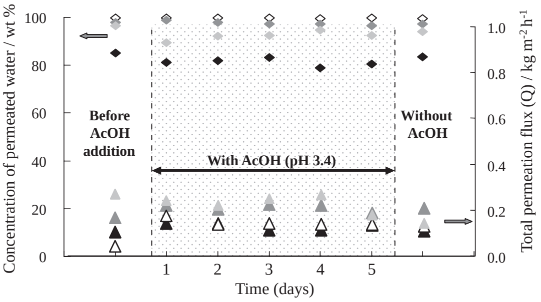

Figure 1. Dehydration performances through the MER membranes at 40 °C in the weight composition of H_2O:EtOH:AcOH = 9:81:10. Triangle: total permeation flux, diamond: concentration of permeated water. Black: H10R, dark grey: M10R, pale grey: L10R, white: L10S.

tion at 40 °C. The XRD patterns showed that MER membranes could be prepared by using synthesis solution with SARs of 1.3–2.5. The obtained membrane surfaces had SARs of 1.5–2.8, as determined by using SEM-EDX. The thickness of the membranes was 10–20 µm. And the macroporous surface of the support could be filled more finely using larger amounts of the seed crystals. As shown in Table 1, the dehydration performances depend on the amounts of the seeds and the SAR. For example, by comparing the performances of 6R1, 6R2, and 6S1, the water separation factor ($\alpha_{W/EtOH}$) increased with the amounts of the seeds. Although the membrane C6 was prepared using the CHA seeds, the dehydration performance agreed with that of the membranes prepared by using the MER seeds. L10R, M10R, and H10R were synthesized using almost the same amounts of the seeds. However, the dehydration performances decreased linearly with increase in the SAR values. These results suggest that the air-tightness in the seeded zone and the hydrophilicity of the membrane were important for the separation mechanism.

To test the water permeation through the MER membranes in an acidic condition with AcOH, 90 wt % EtOH solutions were prepared with and without the addition of AcOH. The former solution was prepared by mixing AcOH in the weight composition of H_2O:C_2H_5OH:AcOH = 9:81:10 (pH 3.4).[7] Then, the membranes L10S, L10R, M10R, and H10R were examined. By comparing the dehydration performances of the solutions with and without AcOH, it was observed that the water permeation through the membranes did not alter significantly, and it was stable for 5 days (Figure 1). Although 3 wt % AcOH was included in the permeates through the H10R, it could not be detected for the L10S, L10R, and M10R. The $\alpha_{w/AcOH}$ value for H10R was 30, respectively. Thus, the MER membranes using the synthesis solutions of SAR = 1.3–1.9 could show high $\alpha_{w/EtOH}$ and $\alpha_{w/AcOH}$.

Table 2 lists the PV performances for 10–90 wt % AcOH solutions. The MER membranes synthesized with low SAR solutions showed higher water selectivity for 50 wt % AcOH solution compared to those for MOR and zeolite T membranes. And the L10S membrane maintained the high separation performances even for a 90 wt % AcOH solution; the AcOH concentration in permeates through the L10S was less than 0.1 wt %. The concentration corresponds to the $\alpha_{w/AcOH}$ value of more than 8000. The permeation flux at 60 °C was 2–3 times larger than that at 40 °C. In the dehydration performance for 90 wt % AcOH solution, the seal of the resin coated with polyimide was broken after 5- or 6-h immersing, however, the MER membrane could be used repeatedly.

Table 2. Dehydration performances of the MER, MOR, and zeolite T membranes for the concentrated AcOH solutions

Zeolite Membrane	Sample Name	AcOH Feed Solution		Permeates	
		Conc. /wt %	Temp. /°C	Conc. of AcOH /wt %	Q /kg m^{-2} h^{-1}
MER	C6	50	60	N.D.[a]	0.9
	6R2	50	40	N.D.[a]	0.4
	L10R	50	40	N.D.[a]	0.4
	L10S	10	40	0.02[b]	0.2
		50		0.04[b]	0.2
		70		0.09[b]	0.2
		90		0.1[b]	0.1
	L10S	50	60	0.01[b]	0.6
MOR[2]		50	80	0.33[c]	0.6
		90		15[c]	0.1>
zeolite T[3]		50	75	0.19[c]	0.9
		90		15[c]	0.1>

[a]Analyzed by GC-TCD. [b]Detected by GC-FID. [c]Calculated from the values of $\alpha_{w/AcOH}$.

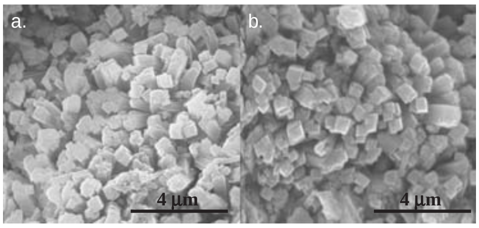

Figure 2. SEM images of the outer surface of the L10R membranes before (a) and after immersing (b) in the 90 wt % AcOH solution at 40 °C for 4.5 days.

The SEM images in Figure 2 shows the outer surface of L10R before and after immersing in the 90 wt % AcOH solution at 40 °C for 4.5 days. The surface images suggest the acid-stability of the MER membrane. By SEM-EDX, the SAR value of L10R surface increased slightly from 1.5 to 1.7 due to dealumination, which imply that L10R was expected to maintain the performance for 90 wt % AcOH solution at 40 °C more than 4 days.

Furthermore, the data in this study shows that we can obtain zeolite membranes with high separation abilities as well as high acid stabilities.

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